Unified Density Functional Theory of Complex Fluids

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I will present a unified density functional theory of complex fluids that is able to take into account thermodynamic nonideality due to both inter- and intra- molecular interactions quantitatively. This density functional theory is based on recent achievements in engineering-oriented statistical-thermodynamic theories of bulk fluids, the statistical associating fluid theory (SAFT) in particular, and a modification of Rosenfeld's fundamental measure theory (FMT) for inhomogeneous hard spheres. The central idea is that the excess Helmholtz energy functional can be approximated by that corresponding to the unbonded monomeric system and an additional term taking into account the effect of bond connectivity on inter-segmental interactions. The excess Helmholtz energy functional for the monomeric system includes contributions from hard-sphere repulsion represented by the modified FMT, from van der Waals attraction calculated from the energy equation using the radial distribution function of bulk fluids, from electrostatic interactions represented by the variational mean-sphere approximation, and from associations represented by an extension of SAFT for inhomogeneous systems. The excess Helmholtz energy functional due to chain connectivity depends on the cavity correlation functions of the monomeric reference fluid. I will discuss applications of the unified density functional theory to structural and thermodynamic properties of various complex fluids including colloids and polymers in the bulk or under confinement.